THE AROMATIC NUCLEOPHILIC SUBSTITUTION REACTION. THE EFFECT OF INITIAL CONCENTRATION ON THE RATE OF THE REACTION OF MOH ON 2,4-DINITROHALOBENZENES

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The rate data for the reaction of hydroxides and activated aryl halides have been sparse. Reports by Bunnett and Davis (1954) and by Reinheimer and Bunnett (1959) contain most of the available data. The data of Bunnett and Davis were for the reaction of NaOH and 2,4-dinitrochlorobenzene. This reaction was run in dioxane-water, and the concentration of the hydroxide was varied. Reinheimer and Bunnett also used dioxane and water as a solvent but their reagents were a series of 2-substituted-4-nitrofluorobenzenes in which the hydroxide concentration was kept constant.

The purpose of the present work was to collect additional data for the nucleophile hydroxide ion. After a few preliminary experiments, it became apparent that the reaction rate constant varied with initial concentration of the hydroxide ion, and also varied with the nature of the cation associated with the hydroxide ion. These results are similar to those of Reinheimer et al (1958). This paper gives the results of a study of the change in the rate constant for the reactions of 2,4-dinitrochlorobenzene and 2,4-dinitrobromobenzene with LiOH, NaOH, KOH and tetrabutyl-ammonium hydroxide, in which the initial concentration of the hydroxide was varied. In addition, a few rate constants for 2,4-dinitroiodobenzene and 2,4-dinitrohalonaphthalenes are reported.

METHODS AND RESULTS

The rate constants for the reaction of 2,4-dinitrohalobenzenes with hydroxide ions were determined in the mixed solvent dioxane-water. The per cent of dioxane had to be sufficiently great to dissolve the activated halide, so that 48.8 per cent by volume was required for 2,4-dinitrohalobenzene and 68 per cent dioxane for 2,4-dinitrochloronaphthalene. Purification of the dioxane was crucial, for the rate constants varied if the solvent was slightly impure. The graph of data for an individual run was excellent, with each point falling on the line. However, if aliquots of the same solutions were used on different days, the rate constant changed from 0.835 to 1.51, 1.54 and 1.97 x 10^{-3} on the first, second, third and sixth days, respectively. Purification of the dioxane by the method of Riddick and Toops (1955) and the use of solvent distilled immediately before use gave reproducible results.

The concentrations for the activated halides were in the range 0.025 to 0.030 M, while that of the hydroxide varied from 0.007 to 0.25 M. This change in hydroxide ion concentration effectively varied the ionic strength of the solution, but requires the use of the following rate expression for equation (1):

$$\frac{dx}{dt} = k_2(a-2x)\ (b-x)$$

where $a = OH^-$ initially
$b = RCl$ initially
$x =$ Halide at time t.

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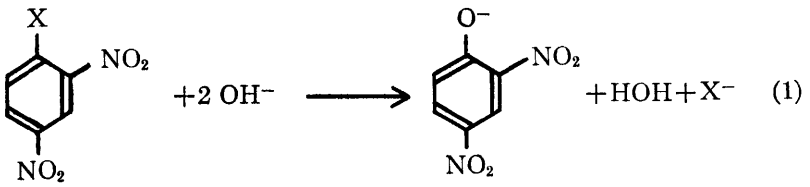
Integrating, one obtains:

$$\frac{1}{(a-2b)} \ln \left(\frac{a-2x}{b-x}\right) o \frac{b}{a} = k_2 t$$



(1)

A plot of $\ln \left(\frac{a-2x}{b-x}\right)$ versus t should give a straight line. The slope of this line was $k_2(a—2b)$ from which the rate constant, k_2, was readily obtained. The rate constants are given in table 1 and the thermodynamic properties of the reaction are displayed in table 2.

TABLE 1

Rate constants for the reaction of 2,4-dinitrohalo compounds with hydroxide ion

Reagent	Concentration (M/1)	Rate Constant (1/mol xsec) $\times 10^{-3}$
*NaOH[a]	0.0074	0.787, 0.795
	0.0135	0.735, 0.762, 0.740
	0.0270	0.722, 0.745, 0.740
	0.0747	0.685, 0.688, 0.681
	0.1256	0.641, 0.640, 0.629
	0.1494	0.634, 0.652, 0.640, 0.629
	0.2511	0.538, 0.539, 0.573, 0.581
*KOH[a]	0.0113	0.947
	0.0312	0.816, 0.849, 0.846
	0.0623	0.769, 0.760
	0.1012	0.737, 0.732
	0.2025	0.718, 0.705
*LiOH[a]	0.0076	0.877, 0.866
	0.0152	0.818, 0.794, 0.781
	0.0254	0.763, 0.769
	0.0381	0.740, 0.721, 0.739
	0.0508	0.720, 0.730
	0.1271	0.672, 0.640, 0.644
	0.2541	0.593, 0.584, 0.584
*NaOH[b]	0.0135	0.540, 0.574
	0.0270	0.505, 0.529, 0.514
	0.0490	0.516, 0.518, 0.530
	0.747	0.487, 0.492, 0.517
	0.1256	0.431, 0.440, 0.450
	0.1494	0.407, 0.430, 0.434
	0.2511	0.354, 0.369, 0.389
*KOH[b]	0.0113	0.638
	0.0312	0.589, 0.559, 0.543
	0.0623	0.513, 0.507
	0.1012	0.486, 0.483
	0.2025	0.463, 0.456
*LiOH[b]	0.0076	0.567, 0.547
	0.0155	0.539, 0.529
	0.0259	0.519, 0.518
	0.0517	0.489, 0.472
	0.1293	0.433, 0.418
	0.2586	0.373, 0.375
**LiOH[a]	0.1295	6.14, 6.26
	0.0648	6.81, 6.74
	0.0259	7.50, 7.42
	0.0130	8.11, 8.05

TABLE 1—*Continued*

Reagent	Concentration (M/1)	Rate Constant (1/mol xsec) $10\times^{-3}$
**KOH[a]	0.1231	6.70, 6.81
	0.0493	7.46, 7.67
	0.0246	8.08, 8.12
	0.0147	8.36, 8.36
**LiOH[b]	0.2586	3.33, 3.47
	0.1293	4.04, 4.00
	0.0517	5.00, 4.80
	0.0259	5.25, 5.09
**KOH[b]	0.1231	4.63, 4.72
	0.0493	5.06, 5.14
	0.0246	5.54, 5.42
	0.0148	5.66, 5.69
*$(C_4H_9)_4NOH$[a]	0.0850	1.61
	0.0425	1.35
	0.0189	1.12, 1.09
*$(C_4H_9)_4NOH$[b]	0.0850	1.03
	0.0425	0.884
	0.0189	0.761, 0.741
**$(C_4H_9)_4NOH$[a]	0.0850	16.3
	0.0425	12.80
	0.0189	10.56, 10.89
**$(C_4H_9)_4NOH$[b]	0.0850	10.5
	0.0425	9.06
*NaOH[c]	0.0149	0.208, 0.204
	0.0270	0.176, 0.167
	0.0747	0.164, 0.167
	0.1494	0.151, 0.150
	0.2511	0.128, 0.132
*KOH[c]	0.0125	0.187, 0.205
	0.0202	0.186, 0.189
	0.0312	0.178, 0.188
	0.0623	0.173, 0.177
	0.1247	0.173, 0.174
	0.2025	0.157, 0.153
*NaOH[d]	0.0508	0.782, 0.795, 0.831, 0.791, 0.825, 0.807, 0.787, 0.820, 0.812, 0.792
*NaOH[e]	0.0508	0.542, 0.520, 0.493, 0.500, 0.506
*NaOH[f]	0.0508	0.168, 0.172, 0.157
**NaOH[d]	0.0508	7.53, 7.55
**NaOH[e]	0.0508	4.89, 4.96
**NaOH[f]	0.0508	1.89, 1.83
NaOH[g,o]	0.0302	1.20, 1.24, 1.20, 1.07
NaOH[h,o]	0.0302	0.815, 0.790
NaOH[i,o]	0.0302	14.41, 13.97, 13.72
NaOH[j,o]	0.0302	8.10
NaOH[g,p]	0.0302	10.9, 11.2, 11.4[n]
NaOH[h,p]	0.0302	7.32, 7.46[n]
NaOH[i,p]	0.0302	107.0, 100.5[n]
NaOH[j,p]	0.0302	53.3
NaOH[k,o]	0.0448	1.069, 1.053, 1.077
NaOH[l,o]	0.0224	1.329, 1.276, 1.273, 1.113
NaOH[l,o]	0.0448	1.058, 0.987
NaOH[m,o]	0.0343	10.022, 9.95, 10.534

*48.8 per cent dioxane and water at 25.0 C.
**48.8 per cent dioxane and water at 49.37 C.
[a]2,4–DNCB = 0.0270.
[b]2,4-DNBB = 0.0270.
[c]2,4–DNIB = 0.0200.
[d]2,4–DNCB = 0.0250.
[e]2,4–DNBB = 0.0250.
[f]2,4–DNIB = 0.0250.
[g]2,4–DNCB = 0.0151.
[h]2,4–DNBB = 0.0151.
[i]2,4–DNCN = 0.0151.
[j]2,4-DNBN = 0.0151.
[k]2,4–DNCB = 0.0224.
[l]2,4–DNCB = 0.0112.
[m]2,4–DNCN = 0.0172.
[n]Solvent expansion factor = 1.03.
[o]68 per cent dioxane and 30 per cent water at 25.0 C.
[p]68 per cent dioxane and 30 per cent water at 49.4 C.

TABLE 2

Thermodynamic properties for the reaction MOH+2,4-dinitrohalobenzenes and 2,4-dinitrohalonaphthalens at 25 C

Reagents[a]	Conc. of MOH (M/1)	ΔE Kcal/mole	ΔH* Kcal/mole	ΔF* Kcal/mole	−ΔS* e.u.
KOH+2,4-DNCB	0.05	17.63	17.03	21.68	15.6
	0.10	17.61	17.01	21.72	15.8
	0.15	17.08	16.48	21.74	17.6
LiOH+2,4-DNCB	0.05	17.75	17.15	21.73	15.4
	0.10	17.62	17.02	21.77	15.9
	0.15	17.50	16.90	21.80	16.4
NaOH+2,4-DNCB	0.05	17.56	16.96	21.67	15 8
KOH+2,4-DNBB	0.05	17.77	17.17	21.92	15.9
	0.10	17.93	17.33	21.96	15.6
	0.15	17.77	17.17	21.99	16.2
LiOH+2,4-DNBB	0.05	18.04	17.44	21.98	15.2
	0.10	17.77	17.17	22.02	16.3
	0.15	17.57	16.97	22.06	17.0
(MOH)+2,4-DNCB	0.00 (k_o)	18.03	17.43	21.57	13.9
(MOH)+2,4-DNBB	0.00 (k_o)	17.45	16.85	21.77	16.5
NaOH+2,4-DNIB[b]	0.05	18.74	18.14	22.59	14.9
NaOH+2,4-DNCB[b]	0.03	17.43	16.83	21.43	15.4
NaOH+2,4-DNBB[b]	0.03	17.39	16.79	21.67	16.4
NaOH+2,4-DNCN[b]	0.03	15.69	15.09	21.34	21.0
NaOH+2,4-DNBN	0.03	14.76	14.16	21.67	25.2
$(C_4H_9)_4NOH$+2,4-DNCB	0.02	17.71	17.11	21.47	14.6
	0.05	17.89	17.30	21.37	13.7
	0.08	17.97	17.37	21.26	13.0
$(C_4H_9)_4NOH$+2,4-DNBB	0.02	18.66	18.07	21.70	12.2
	0.05	18.28	17.69	21.60	13.1
	0.08	18.14	17.55	21.53	13.3

[a]Solvent was 48.8 per cent dioxane by volume unless specified otherwise.
[b]Solvent was 68 per cent dioxane by volume.

As one can see in the graphs II and III, the increasing concentrations for M^+OH^-, ($M = K^+$, Li^+, Na^+), cause a decrease in the rate constant for the reaction. The curves do, however, tend to approach the same rate constant at zero concentration of the OH^-. The curves tend to be somewhat similar in general pattern which does not seem to vary with the change in temperature for the reaction. By following the general shape of the curves of LiOH, NaOH, KOH and by using the tetra-n-butylammonium hydroxide curves, one would estimate that k_o, the rate constant at zero concentration, of the 2,4-dinitrochlorobenzene (DNCB) and M^+OH^- at 25 C to be $0.95 \pm 0.05 \times 10^{-3}$ 1/mole sec, the 2,4-dinitrobromobenzene (DNBB) and M^+OH^- at 25 C to be $0.70 \pm 0.05 \times 10^{-3}$ 1/mole sec, the DNCB and M^+OH^- at 49.4 C to be $9.5 \pm 0.5 \times 10^{-3}$ 1/mole sec, and DNBB and M^+OH^- at 49.4 C to be $6.5 \pm 0.5 \times 10^{-3}$ 1/mole sec.

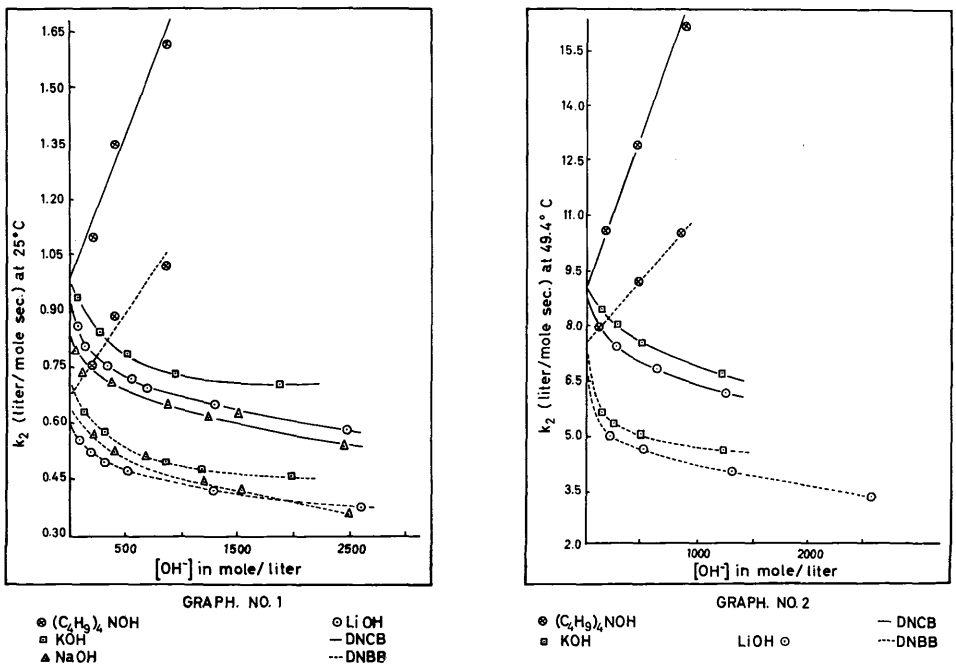
The tetra-n-butylammonium hydroxide and DNXB curves are different from the DNXB and OH^- curves. The rate constant tends to increase rather sharply as the concentration of the $(Bu)_4N^+OH^-$ is increased. This is an unexpected result in view of the other reaction rate curves but is helpful when one determines k_o.

DISCUSSION

The results of our investigation are comparable to those obtained by Bunnett and Davis (1954) for hydroxide ion and DNCB. Their rates in 60 per cent dioxane are 1.0 and 1.1×10^{-3} 1/mole sec at 0.06 and 0.03 M NaOH. Our results were 0.80 and 1.20×10^{-3} 1/mole sec in 48.8 and 68 per cent dioxane with 0.03 M NaOH. They obtained $\Delta E = 17.5$ Kcal/mole and $\Delta S^* - 15.4$ e.u., while our results were $\Delta E = 17.4$ and $\Delta S^* = -15.8$. Their rate decrease with increasing NaOH concentration follows the same pattern as that given in graphs II and III.

Several theories for these observed salt effects are available. The first is

based on the effect of ionic strength on the activity coefficients of the reagents on the transition states (Long, Dunkle, and McDevitt, 1951). Lichtin and Rao (1961) have analyzed the effect of salts on the reaction of Br^- with benzyl bromide in liquid SO_2. Their results are similar to ours with MOH, (where $M=Li^+$, Na^+, K^+), and they argue "The salt effect cannot be simultaneously positive and negative. Accordingly, the variation of k_2 with concentration and the nature of the ionophore cannot be explained in terms of the effect of ionic strength on the activity coefficients of the reactants or transition states." The second is that of the "dual hypothesis" or the reactivity of both the free ion and the ion pair. Acree (1912) utilized these ideas at the turn of the century, while Brandstrom (1957), Lichtin



Graphs No. 1 & 2. Rate constant vs. concentration of the nucleophile for the reaction of 2,4-DNXB $+OH^-$. To obtain experimental rates and concentrations, multiply k_2 by 10^{-3} and [o/t] by 10^{-4}.

and Rao (1961), and Reinheimer, Gerig and Cochran (1961) have applied this hypothesis more recently.

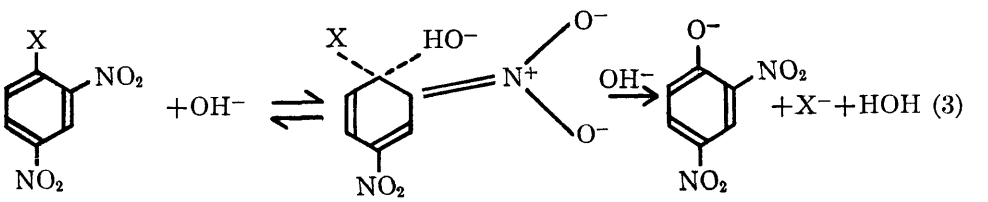
$$k_{obs}=k_i\alpha+(1-\alpha)k_{ip}. \tag{2}$$

If we assume that $k_i>k_{ip}$, (where k_i is rate constant for the ion and k_{ip} is the rate constant for the ion pair and α is the degree of dissociation (M^+, OH^-) then the curves for the alkali metal hydroxides can be rationalized. As the concentration of MOH increased, α decreases, so that the contribution of k_{ip} $(1-\alpha)$ term k_{obs} becomes much larger. The next result is that k_{obs} becomes smaller, for the increase in the second term does not equal the decrease in the first term of equation (2).

Davies (1951) has presented evidence that the alkali metal hydroxides form intimate ion pairs in aqueous solution. The change in dielectric constant to a lower value for the mixed solvent dioxane-water is expected to enhance the degree of ion pairing. No data on the degree of ion pairing in (M^+, OH^-) seems to be

available in the mixed solvent system, so the qualitative estimate must suffice. One obstacle is the somewhat unexpected order of $K^+ > Li^+ > Na^+$ with 2,4-dinitrochlorobenzene at 25 C rather than $K^+ > Na^+ > Li^+$. The latter order is based on the crystallographic ratios and the formation of intimate ion pairs.

However, some precedent for this order is given by the dissociation constants for the alkali metal picrates which show a similar order in the solvent pyridine, Krauss (1958). In pyridine, k_{diss} for lithium picrate is 0.83×10^{-4}, for sodium picrate, 0.43×10^{-4}, and potassium picrate, 1.0×10^{-4}. In acetone, the constants are 10.3, 13.5 and 34.3 respectively. These are metal ion-negatively charged oxygen ion pairs, which should be comparable to the present case. The assignment of a small value for k_{ip} seems reasonable on the basis of the transition state (I) assigned this reaction by Bunnett and Davis (1954), equation (3).



Reinheimer, Gerig and Cochran (1961) have suggested that the ion pair forms an M^+ bond between the OCH_3 and the ortho nitro group in the transition state for the reaction of $MOCH_3$ and 2,4-dinitrochlorobenzene. Bunnett and Morath (1955) have applied the same argument to the transition state for the reaction of piperidine and ortho- or para-chloronitrobenzene. This "built-in solvation" by the ortho group via hydrogen bond can occur in equation 1 with the hydroxide ion, but there is no place for both the H of the OH^- and the M^+ of the (M^+OH^-) ion pairs to fit into this transition state. The oxygen in the nitro group would not be expected to form two hydrogen bond like links.

The rapid increase in rate with increasing concentration for the tetrabutylammonium hydroxide was unexpected. Since this very large cation would not be expected to ion pair readily with any anion (Davies, 1951), one would predict little or no rate change with change of concentration. Stated in other terms, if $k_{ip} = 0$, then k_{obs} would be constant if there were no salt effect on k_i or a small salt effect on k_i. It is difficult to see how $k_{ip} > k_i$ for this system and further why the degree of dissociation would change for this very strong electrolyte. The dual hypothesis does not seem to fit this data. One suggestion is that the addition of salts to water decreases the dielectric constant of the solution (Hasted, Ritson, and Collie, 1948). Since the rate of reaction increased from 0.80 to 1.24×10^{-3} 1/mole sec with a change of dielectric constant from 36 to 18, (48.8 per cent dioxane to 68 per cent dioxane) this change in rate with change in dielectric constant of the solvent is qualitatively correct. The change in dielectric constant of HOH is from 80 to about 70 for 0.5N electrolytes (Hasted, Ritson, and Collie, 1948), while the experimental rate increase which we observe is from 1.0 to 1.9 x 10^{-3} 1/mole sec for a change in concentration of 0 to 0.06M, with tetrabutylammonium hydroxide. If we assume that the rate change is linear with respect to decrease in dielectric constant, the change in rate observed calls for a change in dielectric constant of twice that observed, i.e., about 36. This seems to be too great a change to be accounted for by the modest increase in salt concentration.

Overall, the large rate constant increases with increasing tetrabutyl-ammonium hydroxide concentration are somewhat similar to the salt effects observed by Winstein and Clippinger (1956) and Winstein and Robinson (1958). They attribute the straight line portion of their curve to "normal salt effects, which occur above a concentration of about 0.01M." However, there seems to be no "special

salt effect," for our extrapolated curves approach the same limiting value from above and below.

The assignment of the role "normal salt effects" to the tetrabutyl-ammonium hydroxide reagent would require that the sign of the salt effect be positive. If this is correct, then the salt is accelerating a reaction between two ions which have the same charge. This would mean that the second step of the intermediate complex mechanism, the attack of OH^- on the negatively charged transition state, is affected by the tetrabutyl-ammonium hydroxide. This seems reasonable, for larger salt effects are expected for reactions between ions than between an ion and a dipolar molecule. This conclusion leads to the prediction that the salt effect of tetrabutyl-ammonium methoxide on its reaction with 2,4-dinitrochlorobenzene would be much smaller than in the present case, for there is no attack by a negative ion on a negative transition state to form the products.

EXPERIMENTAL

Purification of 1-chloro-2,4-dinitrobenzene

The Eastman white label 2,4-DNCB was used throughout this experimental work. It was recrystallized from ether at least twice or until the melting point range was 50 to 51 C. Literature value is 50 to 53.4 C (Lange 1956) depending on the form.

Purification of 1-bromo-2,4-dinitrobenzene

Eastman white label 2,4-DNBB was recrystallized at least twice from ether or until the melting point range was 71 to 72 C. Literature value is 70.6 to 75.3 C (Beilstein 1922) depending on the form.

Preparation of 1-iodo-2,4-dinitrobenzene

This was accomplished by the procedure of Bunnett and Conner (1958). The melting point of our product was 88.5 to 89.5 C, in agreement with the literature value.

Purification of 1,4-dioxane

Dioxane proved to be one of the problems in the kinetic runs. Commercial grade dioxane was used and unless it was purified carefully and completely the rate constants increased from run to run. The first purification method was to add sodium to the dioxane, reflux until the sodium was bright and then distill it from the sodium. When the rate constants for a reaction on succeeding runs increased 2 to 3 times, a new method was looked for quickly. The method (Riddick and Toops, 1955), finally used was to boil the dioxane under reflux for 7 hours with 10 per cent of its volume of 1 N HCl, passing a slow stream of air through the condenser to remove acetaldehyde. To remove the water, the dioxane was treated with NaOH and the aqueous layer removed. It was then allowed to stand over NaOH for one day and then refluxed over sodium until the sodium was bright (usually 6 to 12 hr). Finally it was distilled from sodium using a silvered, vacuum jacketed, 24-inch column packed with glass helices. Even this procedure must be done carefully to get the best results.

Standardization of NaOH

Certified Fisher 5N sodium hydroxide was diluted to the approximate desired normality with distilled water. This was standardized against potassium-acid phthalate.

Standardization of KOH

Fisher ACS pellets of potassium hydroxide were dissolved in distilled water to make the desired strength solution. Ten grams of calcium hydroxide was added and the resulting mixture stirred with a magnetic stirrer for one hr, while the mixture was protected from the carbon dioxide in the air. This carbonate-

free KOH was filtered through a fine sintered-glass funnel and then standardized with KHP as described in the NaOH standardization.

Standardization of LiOH

Matheson, Coleman, and Bell lithium hydroxide reagent crystals were used. To remove the carbonate a saturated solution (110 g/liter) was made and allowed to stand for several hours. The carbonate, not being as soluble, settled and was filtered off using a fine sintered-glass funnel. KHP was used to standardize the solution.

Preparation and standardization of tetra-n-butyl-ammonium hydroxide

Titration grade was purchased from Southwestern Analytical Chemicals. After being standardized we used it for some kinetics runs but found that there was some unknown impurity present that give different initial and final rates. An article by Fritz and Marpel (1962) suggested to us that amines might be the problem so we added 20 per cent of pure benzene to our solution, shook it vigoroulsy, and let it stand until the two phases separated completely. This solution was then passed through a column of 20 grams of strong base anion exhange resin in the hydroxide form, Amberlite 400, and restandardized. Kinetic runs were again attempted with the same results as before.

We prepared our tetra-n-butyl-ammonium hydroxide by the method of Fritz and Marple (1962). We used a rotary vacuum evaporator to remove the methanol. We found that the tetra-n-butyl-ammonium hydroxide was far less soluble than implied by Fritz, and that it precipitated out readily. We were able to prepare an 0.18 M solution in water, however. The hydroxide was standardized against potassium acid phthalate.

Kinetic proceudure

Preparation of solutions.—The purified DNXB and DNXN compounds were weighed out on an analytical balance and then dissolved in 50.0 ml dioxine. The solution was then diluted to the mark with distilled water.

The standardized hydroxide solution was added to 50.0 ml of dioxane, and thoroughly shaken. The amount of hydroxide solution added depended upon the final concentration desired. Water was added to finish filling up the volumetric flask when needed. Final concentrations were 48.8 and 68% dioxane by volume.

Mixing.—Fifty ml of each of the two solution, DNXB or DNXN and (OH^-), were pipetted into separate standard taper 300-ml round-bottom flasks. The two flasks were then connected with a curved adapter, the contents of one flask poured into the other and back again several times before returning the one flask and all the contents to the bath.

Sampling.—10-ml samples were pipetted from the reaction flask at the proper times. These samples were put into 100-ml beakers which contained an acid stopping solution, (Dilute HoAc or dilute HNO_3), and distilled water. Eight samples were taken from each run.

Timing.—The timing was started for the kinetics runs when, in the mixing stage, half the contents of one flask had emptied into the second flask. The timing itself was done by a precision timer, a "Time-It," to the nearest second. The recorded time for each 10–ml sample was taken when half of the sample had flowed from the pipette into the beaker with its stopping solution.

Titrating.—Standardized silver nitrate was used for determining the amount of the halide present in the solution by means of a potentiometric titration. Two calibrated burets were used. One of these carried 0.05 ml graduations and the other 0.02 ml.

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